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APPLICANTS: Kazutaka Habu et al.

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FILING DATE: April 28, 1998   GROUP ART UNIT: 1742

TITLE: SOLDER MATERIAL   EXAMINER: S.Ip

Hon. Commissioner of Patents and Trademarks,
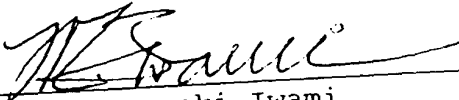   Washington, D.C. 20231

S I R:

CERTIFIED TRANSLATION

I, Masaaki Iwami of 3-22, Asagaya-minami 1-chome, Suginami-ku, Tokyo, Japan, am an experienced translator of the Japanese language into the English language and I hereby certify that the attached comprises an accurate translation into English of Japanese Patent Application No. Hei 09-348212, filed on December 17, 1997.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

8th October, 1999

_____   _____
Date   Masaaki Iwami

[Name of Document]   Specification

[Title of the Invention]

Solder Material

[What is Claimed is]

[Claim 1] A solder material composed of a Sn-Zn-Bi alloy containing 0.5 to 10 wt% of zinc and 0.5 to 8 wt% of bismuth, the balance being substantially tin, characterized in that

0.005 to 0.05 wt% of germanium and 0.3 to 3 wt% of copper are added to said Sn-Zn-Bi alloy.

[Claim 2] A solder material composed of a Sn-Bi-Ag alloy containing 0.5 to 8 wt% of bismuth and 0.5 to 3 wt% of silver, the balance being substantially tin, characterized in that

0.01 to 0.1 wt% of germanium is added to said Sn-Bi-Ag alloy.

[Claim 3] A solder material according to claim 2, wherein 0.3 to 1 wt% of copper is further added to said Sn-Bi-Ag alloy.

[Claim 4] A solder material composed of a Sn-Zn-In alloy containing 3 to 15 wt% of zinc and 3 to 10 wt% of indium, the balance being substantially tin, characterized in that

0.01 to 0.3 wt% of germanium and 0.3 to 3 wt% of

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silver are added to said Sn-Zn-In alloy.

[Detailed Description of the Invention]

[0001]

  [Technical Field to Which the Invention Pertains]

    The present invention relates to a solder material used for connection of various electronic parts to be mounted on a circuit board.

[0002]

  [Related Art]

    A tin-lead based alloy having an eutectic composition of tin and lead has been mainly adopted as a solder material used for connection of various electronic parts to be mounted to a circuit board.

[0003]

    Recently, mainly in Europe and the United States of America, a problem associated with environmental pollution due to lead has been pointed out, and discussion has been actively made to legislate the regulation for limiting the use of lead. To cope with such a trend, it has been examined to reduce the amount of lead contained in the conventional lead based solder material or it has been required to develop a lead-less solder material.

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[0004]

The tin-lead based solder material most popularized at present has an eutectic composition of 63 wt% of tin and 37 wt% of lead, which has an eutectic temperature of 183°C. In such a tin-lead solder material, the wettability is optimized by adjusting the composition ratio of lead in such a manner as to be good at a low temperature. The tin-lead solder material, therefore, exhibits a desirable solderability at a low temperature.

[0005]

On the other hand, a lead-less solder material having been examined at present contains tin as a basic component, and further contains a plurality of elements to obtain characteristics comparable to those of the tin-lead based solder material. To be more specific, the characteristics of the lead-less solder material is controlled by adding various additional elements to a binary eutectic alloy such as a Sn-Ag, Sn-Zn, Sn-In, or Sn-Bi based alloy.

[0006]

[Problem to be Solved by the Invention]

The above lead-less solder material, however, is inferior to the tin-lead solder material in terms of temperature characteristics such as melting temperature

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and wettability, and is expected to be further improved in its characteristics.

[0007]

In particular, the grade of the solderability of a solder material is dependent on the wettability of the solder material. To be more specific, if the solder material is less wetted, there occurs a failure in contact with a material to be joined, while if the solder material is excessively wetted, a bridge of solder is formed between materials not to be joined, resulting in short-circuit therebetween. The problem associated with the wettability becomes more serious as the mounting density of a circuit board becomes higher. It is not too much to say that the quality of electronic parts in surface mounting is determined by the wettability of a solder material.

[0008]

From the above viewpoint, since the lead-less solder material having been proposed does not contain lead, it is difficult to control the wettability and hence to obtain a desirable solderability.

[0009]

In view of the foregoing, the present invention has been proposed, and an object of the present invention is

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to provide a lead-less solder material having a good wettability leading to a desirable solderability.

[0010]

　[Means for Solving the Problem]

　　　To achieve the above object, according to the present invention, there is provided a solder material composed of a Sn-Zn-Bi alloy containing 0.5 to 10 wt% of zinc and 0.5 to 8 wt% of bismuth, the balance being substantially tin, characterized in that 0.005 to 0.05 wt% of germanium and 0.3 to 3 wt% of copper are added to said Sn-Zn-Bi alloy.

[0011]

　　　According to the present invention, there is provided a solder material composed of a Sn-Bi-Ag alloy containing 0.5 to 8 wt% of bismuth and 0.5 to 3 wt% of silver, the balance being substantially tin, characterized in that 0.01 to 0.1 wt% of germanium is added to said Sn-Bi-Ag alloy. In this solder material, 0.3 to 1 wt% of copper may be further added to said Sn-Bi-Ag alloy.

[0012]

　　　According to the present invention, there is provided a solder material composed of a Sn-Zn-In alloy containing 3 to 15 wt% of zinc and 3 to 10 wt% of indium,

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the balance being substantially tin, characterized in that 0.01 to 0.3 wt% of germanium and 0.3 to 3 wt% of silver are added to said Sn-Zn-In alloy.

[0013]

Since each of the solder material composed of the Sn-Zn-Bi alloy to which Ge and Cu are added, the solder material composed of the Sn-Bi-Ag alloy to which Ge is added, and the solder material composed of the Sn-Bi-Ag alloy to which Ge and Cu are added has a melting temperature being substantially the same as that of the tin-lead alloy and has good mechanical properties. In particular, by adding germanium, copper or silver as the additional element, the wettability is improved and thereby a desirable solderablity can be obtained.

[0014]

[Mode for Carrying Out the Invention]

Hereinafter, embodiments of the present invention will be described.

[0015]

The solder material of the present invention is a lead-less solder material containing Sn as a basic element, and more specifically, it is composed of: (1) a Sn-Zn-Bi alloy containing tin, zinc, and bismuth to which germanium and copper are added; (2) a Sn-Bi-Ag alloy

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containing tin, bismuth, and silver to which germanium is added, or a Sn-Bi-Ag alloy to which germanium and copper are added; and (3) a Sn-Zn-In alloy containing tin, zinc, and indium to which germanium and silver are added.

[0016]

Each of Ge, Cu, and Ag added to the solder material as additional elements is used for improving the wettability of the solder material.

[0017]

However, to improve the wettability of the solder material and to obtain the good solderability thereof, it is required not only to use the above additional elements but also to set the composition ratio of each element contained in the solder material in a suitable range. The suitable composition ratio of each element contained in each of the above solder materials will be described below. In addition, the composition ratio (wt%) of each element contained in the solder material is determined on the basis of the result of measuring a molten solder sample by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometer) analysis.

[0018]

(1) For the solder material composed of the Sn-Zn-Bi alloy to which Ge and Cu are added, the composition

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ratio of each element is required to be in the following range:

[0019]

Zn: 0.5 to 10 wt%

Bi: 0.5 to 8 wt%

Ge: 0.005 to 0.05 wt%

Cu: 0.3 to 3 wt%

Sn: balance

Of the above elements, Zn and Bi function to lower the melting temperature of the solder material. If Zn or Bi is less than the above range, the melting temperature of the solder material becomes higher than that of, for example, the tin-lead solder, to cause an inconvenience that the solder material cannot be practically used in accordance with the existing soldering process. If Zn or Bi is more than the above range, the solder material becomes brittle, tending to cause disconnection and the like. Further, as the composition ratio of Zn or Bi becomes larger, the flowability of the solder material tends to become smaller. Additionally, the composition ratio of Zn is preferably in a range of 0.5 to 5 wt%, and the composition ratio of Bi is preferably in a range of 0.5 to 3 wt%.

[0020]

Ge and Cu are added to improve the wettability of the solder material. If Ge or Cu is out of the above range, the wettability is reduced, with a result that it is impossible to obtain the good solderability. In particular, Cu functions to assist incorporation of Ge in the solder alloy. If Cu does not coexist with Ge, it is difficult to incorporate a sufficient amount of Ge in the solder alloy. Accordingly, even to obtain the additional effect of Ge, it is required to add Cu in the solder alloy.

[0021]

However, if the composition ratio of Cu is more than the above range, an intermetallic compound of Cu and Sn is formed, thereby tending to cause cracks. Further, if the added amount of Cu becomes excessively larger, the melting temperature of the solder material becomes higher than that of the tin-lead solder, thereby causing an inconvenience that the heating temperature of the solder material upon connection of electronic parts must be set at a high value.

[0022]

(2) For the Sn-Bi-Ag alloy to which Ge is added, the composition ratio of each element is required to be in the following range:

[0023]

Bi: 0.5 to 8 wt%

Ag: 0.5 to 3 wt%

Ge: 0.01 to 0.1 wt%

Sn: balance

Of the above elements, Bi functions to lower the melting temperature of the solder material. If the composition ratio of Bi is less than the above range, the melting temperature of the solder material becomes higher than that of the tin-lead alloy, thereby causing an inconvenience that the heating temperature of the solder material upon connection of electronic parts must be set at a high value. Further, if the composition ratio of Bi is less than 0.5 wt%, the wettability of the solder material is degraded. On the other hand, if the composition ratio of Bi is more than the above range, the solder material becomes brittle, tending to cause disconnection and the like.

[0024]

Ag is used for controlling the wettability of the solder material. If the composition ratio of Ag is in the above range, the contact angle θ measured in the wetting balance test to be described later is small, and thereby the good wettability is ensured; however, if the

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composition ratio of Ag is out of the above range, the wettability is degraded. Further, if the added amount of Ag becomes large, the melting temperature of the solder material becomes excessively large, or acicular crystals are precipitated to deteriorate the mechanical properties of the solder material.

[0025]

Ge is added for improving the wettability of the solder material. If the composition ratio of Ge is out of the above range, the wettability is degraded, with a result that it is impossible to obtain the good solderability. Further, Ge functions to suppress occurrence of oxides called dross.

[0026]

Cu may be added together with Ge to the Sn-Bi-Ag alloy. In this case, the composition ratio of Cu is required to be in the following range:

[0027]

Cu: 0.3 to 1 wt%

Cu functions to improve the wettability of the solder material and also to assist incorporation of Ge in the solder material. Accordingly, even to control the composition ratio of Ge, it is advantageous to add Cu in the solder alloy. However, if the composition ratio of Cu

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is more than the above range, an intermetallic compound
of Cu and Sn is formed, thereby tending to cause cracks.
Further, if the added amount of Cu becomes excessively
large, the melting temperature of the solder material
becomes higher than that of the tin-lead solder, to cause
an inconvenience that the wettability is degraded.
[0028]

(3) For the Sn-Zn-In alloy to which Ge and Ag are
added, the composition ratio of each element is required
to be in the following range:
[0029]

Zn: 3 to 15 wt%

In: 3 to 10 wt%

Ge: 0.01 to 0.3 wt%

Ag: 0.3 to 3 wt%

Sn: balance

Of the above elements, Zn functions to lower the
melting temperature of the solder material. If the
composition ratio of Zn is less than the above range, the
melting temperature of the solder material becomes higher
than that of the tin-lead solder, thereby causing an
inconvenience that the heating temperature of the solder
material upon connection of electronic parts must be set
at a high value.

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[0030]

Additionally, the composition ratio of Zn is preferably in a range of 6 to 10 wt%.

[0031]

The element In functions to improve the wettability of the solder material and also to lower the melting temperature thereof. If the composition ratio of In is less than the above range, the wettability is degraded or the melting temperature becomes excessively high, with a result that it is impossible to obtain the good solderability. If the composition ratio of In is more than the above range, the mechanical strength of the solder material tends to be weakened.

[0032]

Ge and Ag function to improve the wettability of the solder material. If the composition ratio of Ge or Ag is less than the above range, the wettability becomes insufficient, with a result that it is impossible to obtain the good solderability. If the composition ratio of Ag is more than the above range, the wettability is degraded and the melting temperature of the solder material becomes excessively high. Even in this case, the upper limit of the composition ratio of Ge is equivalent to the maximum value of the amount incorporated in the

solder alloy, and therefore, it is naturally determined on the basis of the above maximum value.

[0033]

The composition ratio of each element contained in the solder material of the present invention is specified as described above. Additionally, with respect to the composition of the solder material, the wording "the balance being substantially tin" means that the balance is mainly composed of Sn and may contain inevitable impurities.

[0034]

The above-described solder material is obtained by a method wherein grains or an ingot of tin as a ground metal and grains or ingots of other elements as ground metals are charged in a crucible, and melted and cooled, to be solidified (alloyed).

[0035]

For Sn, Zn, Bi, Ag, and In as the elements of a solder alloy, the mixing ratio between the amounts of the elements to be charged in a crucible is substantially equivalent to the ratio between the amounts of the elements contained in the solder alloy, and therefore, the amount corresponding to the composition ratio of each element may be regarded as the amount of the element to

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be charged in the crucible.

[0036]

On the other hand, for Cu and Ge, if a ground metal of the single element Cu or Ge is used, part of the charged amount of the element is not alloyed and remains in a crucible. In the case of Cu, the ratio of the amount incorporated in the alloy to the charged amount is about 70%; and in the case of Ge, the ratio of the amount incorporated in the alloy to the charged amount becomes significantly smaller than 70%, for example, about 1% for a Sn-Zn-Bi alloy and about 10% for a Sn-Bi-Ag alloy or a Sn-Zn-In alloy. The amount of each of Cu and Ge to be charged must be thus set in consideration of the above-described loss. In addition, the incorporation of Ge in the alloy is promoted by the coexistence of Cu. For example, if Cu is added together with Ge, the incorporated amount of Ge in the alloy becomes about several times that in the case where only Ge is added.

[0037]

[Examples]

Hereinafter, examples of the present invention will be described on the basis of experimental results.

[0038]

In Inventive Example 1-1 and Comparative Examples

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1-1 to 1-5, the effects of additional elements added to a Sn-Zn-Bi alloy were examined; in Inventive Examples 2-1 and 2-2 and Comparative Examples 2-1 and 2-2, the effects of additional elements added to a Sn-Bi-A_j alloy were examined; and in Inventive Example 3-1 and Comparative Examples 3-1 to 3-6, the effects of additional elements added to a Sn-Zn-In alloy were examined.

[0039]

<u>Inventive Example 1-1</u>

Granular ground metals of tin, zinc, bismuth, germanium, and copper were weighed in predetermined amounts shown in Table 1, and were mixed and charged in a magnetic crucible having a volume of 5 cc. Each of the granular ground metal has a purity of 99.99% or more. The ground metals were melted at about 400℃, being kept in the melting state for 2 to 3 hr, and cooled. A solder ingot (solder sample composed of a Sn-Zn-Bi alloy to which Ge and Cu were added) was thus prepared. The composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 2.

[0040]

<u>Comparative Example 1-1</u>

Granular ground metals of tin, zinc, and bismuth were weighed in predetermined amounts shown in Table 1,

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and charged in the crucible. The ground metals were then melted and cooled in the same manner as that in Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Zn-Bi alloy to which any additional element was not added) was thus prepared. In addition, the composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 2.

[0041]

Comparative Example 1-2

Granular ground metals of tin, zinc, bismuth, and germanium were weighed in predetermined amounts shown in Table 1, and charged in the crucible. The ground metals were then melted and cooled in the same manner as that in Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Zn-Bi alloy to which Ge was added) was thus prepared. In addition, the composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 2.

[0042]

Comparative Example 1-3

Granular ground metals of tin, zinc, bismuth, and silver were weighed in predetermined amounts shown in Table 1, and charged in the crucible. The ground metals were then melted and cooled in the same manner as that in

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Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Zn-Bi alloy to which Ag was added) was thus prepared. In addition, the composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 2.

[0043]

Comparative Example 1-4

Granular ground metals of tin, zinc, bismuth, germanium, and silver were weighed in predetermined amounts shown in Table 1, and charged in the crucible. The ground metals were then melted and cooled in the same manner as that in Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Zn-Bi alloy to which Ge and Ag were added) was thus prepared. In addition, the composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 2.

[0044]

Comparative Example 1-5

Granular ground metals of tin, zinc, bismuth, germanium, silver, and copper were weighed in predetermined amounts shown in Table 1, and charged in the crucible. The ground metals were then melted and cooled in the same manner as that in Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Zn-Bi

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alloy to which Ge, Cu, and Ag were added) was thus prepared. In addition, the composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 2.

[0045]

[Table 1]

	Sn (wt%)	Zn (wt%)	Bi (wt%)	Ge (wt%)	Ag (wt%)	Cu (wt%)
Inventive Example 1-1	88.3	8.7	2.0	0.5	0.0	0.5
Comparative Example 1-1	89.8	8.7	2.0	0.0	0.0	0.0
Comparative Example 1-2	88.8	8.7	2.0	0.5	0.0	0.0
Comparative Example 1-3	88.8	8.7	2.0	0.0	0.5	0.0
Comparative Example 1-4	88.3	8.7	2.0	0.5	0.5	0.0
Comparative Example 1-5	87.8	8.7	2.0	0.5	0.5	0.5

[0046]

[Table 2]

	Sn (wt%)	Zn (wt%)	Bi (wt%)	Ge (wt%)	Ag (wt%)	Cu (wt%)
Inventive Example 1-1	balance	9.2	2.0	0.03	0	0.37
Comparative Example 1-1	ditto	9.0	2.0	0	0	0
Comparative Example 1-2	ditto	9.3	1.9	0.006	0	0
Comparative Example 1-3	ditto	9.2	2,0	0	0.5	0
Comparative Example 1-4	ditto	9.6	2.0	0.08	0.6	0
Comparative Example 1-5	ditto	9.3	2.0	0.03	0.5	0.36

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[0047]

The wettability of each solder sample thus prepared was evaluated by the wetting balance test.

[0048]

In the wetting balance method, the wettability of a solder is evaluated by dipping a base material (to be joined) in the molten solder, and observing a change in wet force F with elapsed time (transient phenomenon).

[0049]

The wet force F is obtained by the following equation:

[0050]

$$F = \gamma \cdot L \cdot \cos\theta - g \cdot \rho \cdot V$$

F: wet force

γ: surface tension

L: length of periphery of base material in molten solder

θ: contact angle between base material and molten solder

ρ: density of molten solder

V: volume of base material in molten solder

g: gravitational acceleration

A curve shown in Fig. 1 is obtained by dipping the base material in the molten solder at a specific velocity and observing a change in wet force F with elapsed time

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after contact of the base material with the molten solder.

[0051]

The wettability of the solder can be evaluated from the curve shown in Fig. 1. To be more specific, a time (zero cross time) Tb elapsed from a time point at which the base material is brought into contact with the molten solder to a time point at which the wet force becomes zero, a rising gradient after the wet force becomes positive, and a stable wet force F_2 when the solder gets sufficiently wet against the base material and thereby the wet force becomes constant, are taken as factors determining the wettability of the solder. Concretely, as the zero cross time Tb is shorter, the rising gradient of wet force is steeper, and the stable wet force F_2 is larger, the wetting/spreading speed of the solder is higher. Such a high wetting/spreading speed of the solder means a desirable wettability of the solder.

[0052]

The changes in wet force with elapsed time were observed for the solder samples prepared in Inventive Examples 1-1 and Comparative Examples 1-1 to 1-5. The results are shown in Figs. 2 and 3. To be more specific, the wettabilities of the solder samples in Inventive Example 1-1 and Comparative Example 1-1 are shown in Fig.

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2, and the wettabilities of the solder samples in Comparative Examples 1-1 to 1-5 are shown in Fig. 3. In addition, the measurement conditions were set as follows:

[0053]

   *base material (to be joined): copper wire having outside diameter of 0.6 mm (subjected to surface treatment by pure rosin based flux)

   *surface temperature of molten solder: about 240℃ (238± 3℃)

   *feed velocity of copper wire into solder bath: 10 mm/sec

   *dipped depth of copper wire: 2 mm

   *holding time of copper wire in solder bath: 10 sec

      As is apparent from Fig. 2, when compared with the solder sample in which Ge and Cu are not added, the solder sample in which Ge and Cu are added is somewhat poor in wet force F_2; however, it exhibits a short zero cross time Tb and a steep rising gradient of wet force, and therefore, it exhibits a good wettability as a whole.

[0054]

      As a result, it becomes apparent that for the Sn-Zn-Bi based solder sample, the addition of Ge and Cu is effective to improve the wettability.

[0055]

Fig. 3 shows not only the wettability of the solder sample in which any additional element is not added but also the wettabilities of the solder sample in which Ge is singly added, the solder sample in which Ag is singly added, the solder sample in which Ag and Ge are added, and the solder sample in which Ag, Ge and Cu are added.

[0056]

Of the above solder samples, the solder sample in which Ag is singly added and the solder sample in which Ag, Ge and Cu are added are significantly poor in wettability. For the solder sample in which Ag and Ge are added, the zero cross time Tb and the rising gradient of wet force are substantially comparative to those of the solder sample in which any additional element is not added, and the stable wet force F_2 is lower than that of the solder sample in which any additional element is not added. For the solder sample in which Ge is singly added, either of the zero cross time Tb, the rising gradient of wet force, and the wet force F_2 is poorer than that of the solder sample in which any additional element is not added.

[0057]

As a result, it becomes apparent that the wettability of the Sn-Zn-Bi based solder sample is rather

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degraded by singly adding Ge or Cu, or adding Ge or Cu in combination of another element, and the effect of improving the wettability of the Sn-Zn-Bi based solder sample is obtained only by adding the two elements Ge and Cu.

[0058]

In addition, Table 2 shows the amount of each element to be charged in each of Inventive Example 1-1 and Comparative Examples 1-1 to 1-5, and Table 3 shows the amount of each element contained in the alloy in each of Inventive Example 1-1 and Comparative Examples 1-1 to 1-5.

For the element Ge, a large difference occurs between the amount of Ge to be charged and the amount of Ge contained in the alloy. This means that it is relatively difficult to incorporate Ge in the alloy. In comparison of Comparative Example 1-2 in which Ge is singly added with Inventive Example 1-1 in which Ge and Cu are added, the amount of Ge to be charged in Inventive Example 1-1 is the same as that in Comparative Example 1-2; however, the amount of Ge contained in the alloy in Inventive Example 1-1 is larger than that in Comparative Example 1-2. This teaches that Cu functions to assist the incorporation of Ge in the alloy.

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[0059]

Inventive Example 2-1

Granular ground metals of tin, bismuth, silver and germanium were weighed in predetermined amounts shown in Table 3, and charged in the crucible. The ground metals were then melted and cooled in the same manner as that in Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Bi-Ag alloy to which Ge was added) was thus prepared. In addition, the composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 4.

[0060]

Inventive Example 2-2

Granular ground metals of tin, bismuth, silver, germanium, and copper were weighed in predetermined amounts shown in Table 3, and charged in the crucible. The ground metals were then melted and cooled in the same manner as that in Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Bi-Ag alloy to which Ge and Cu were added) was thus prepared. In addition, the composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 4.

[0061]

Comparative Example 2-1

Granular ground metals of tin, bismuth, and silver
were weighed in predetermined amounts shown in Table 3,
and charged in the crucible. The ground metals were then
melted and cooled in the same manner as that in Inventive
Example 1-1. A solder ingot (solder sample composed of a
Sn-Bi-Ag alloy to which any additional element was not
added) was thus prepared. In addition, the composition of
the solder sample, measured by the ICP-AES analysis, is
shown in Table 4.

[0062]

Comparative Example 2-2

Granular ground metals of tin, bismuth, silver, and
copper were weighed in predetermined amounts shown in
Table 3, and charged in the crucible. The ground metals
were then melted and cooled in the same manner as that in
Inventive Example 1-1. A solder ingot (solder sample
composed of a Sn-Bi-Ag alloy to which Cu was added) was
thus prepared. In addition, the composition of the solder
sample, measured by the ICP-AES analysis, is shown in
Table 4.

[0063]

[Table 3]

	Sn (wt%)	Bi (wt%)	Ag (wt%)	Ge (wt%)	Cu (wt%)
Inventive Example 2-1	93.5	4.0	2.0	0.5	0.0
Inventive Example					

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2-2	93.0	4.0	2.0	0.5	0.5
Comparative Example 2-1	94.0	4.0	2.0	0.0	0.0
Comparative Example 2-2	93.5	4.0	2.0	0.0	0.5

[0064]

[Table 4]

	Sn (wt%)	Bi (wt%)	Ag (wt%)	Ge (wt%)	Cu (wt%)
Inventive Example 2-1	balance	4.1	2.1	0.04	0
Inventive Example 2-2	ditto	4.1	2.0	0.07	0.51
Comparative Example 2-1	ditto	4.0	2.0	0	0
Comparative Example 2-2	ditto	4.0	2.0	0	0.50

[0065]

The wettability of each solder sample thus prepared was evaluated in the same manner as that described above by the wetting balance method. The results are shown in Fig. 4.

[0066]

As is apparent from Fig. 4, for each of the solder sample composed of the Sn-Bi-Ag alloy to which Ge is added and the solder sample composed of the Sn-Bi-Ag alloy to which Ge and Cu are added, the zero cross time Tb is shorter, the rising gradient of wet force is steeper, and the wet force F_2 is larger as compared with the solder sample composed of the Sn-Bi-Ag alloy to which

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Ge and Cu are not added. In particular, for the solder sample in which Ge and Cu are added, the wet force F_2 is large.

[0067]

Fig. 4 also shows the wettability of the solder sample in which Cu is singly added. The solder sample in which Cu is singly added exhibits the rising gradient of wet force which is slightly steeper than that of the solder sample in which any additional element is not added, but is gentler than that of each of the solder sample in which Ge is added and the solder sample in which Ge and Cu are added.

[0068]

As a result, it becomes apparent that to improve the wettability of the solder sample, it is effective to add single Ge or both Ge and Cu to the Sn-Bi-Ag alloy based solder material.

[0069]

Each of the solder samples in Inventive Examples 2-1 and 2-2 and Comparative Examples 2-1 and 2-2 was then subjected to another test of examining the occurrence of oxides called dross. In this test, each sample was soldered by the flow using a dipping bath (temperature: 260°C, dipping time: 1 hr). As a result, for the solder

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sample in which Ge is added, the generated amount of dross becomes 40-50% of that for the solder sample in which any additional element is not added. This shows that the addition of Ge is effective to prevent occurrence of dross.

[0070]

Tables 3 and 4 show the charged amount and the alloyed amount of each element for each of the solder samples in Inventive Examples 2-1 and 2-2 and Comparative Examples 2-2 and 2-2, respectively. Even in these solder samples, like the Sn-Zn-Bi based solder samples, the alloyed amount of Ge is smaller than the charged amount thereof. Further, in comparison of Inventive Example 2-2 in which Ge and Cu are added with Inventive Example 2-1 in which Ge is singly added, the charged amount of Ge in Inventive Example 2-2 is the same as that in Inventive Example 2-1; however, the alloyed amount of Ge in Inventive Example 2-2 is larger than that in Inventive Example 2-1. This teaches that even in the Sn-Bi-Ag alloy, Cu functions to assist the incorporation of Ge in the alloy.

[0071]

Examination of Composition of Sn-Bi-Ag Alloy to Which Ge and Cu are Added

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As described above, of the Sn-Bi-Ag based alloys, the Sn-Bi-Ag alloy to which Ge and Cu are added exhibits the most preferable wettability. Next, the suitable composition range of the Sn-Bi-Ag alloy to which Ge and Cu are added will be examined.

[0072]

A ground metal of tin containing germanium in an amount of several %, and ground metals of bismuth, germanium, and copper were weighed in specific amounts, and were mixed and charged in a crucible. The ground metals were melted and cooled in the same manner as that in Inventive Example 1-1, to produce a solder ingot. In this way, several kinds of solder samples were prepared by taking a composition of 4wt%Bi-2wt%Ag-0.1wt%Ge-0.5wt%Cu as the basic composition and changing either of elements Bi, Ag, Ge, and Cu of the basis composition. In addition, the reason why the ground metal of tin containing germanium is used is to suppress an error in incorporation of Ge into the solder alloy.

[0073]

For each solder sample thus prepared, the wettability was examined by the above-described wetting balance method and the breaking impact energy was also examined.

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[0074]

The breaking impact test is performed by dropping a base material having a soldered portion from a variable height. In this test, a height causing breakage of the soldered portion is taken as a drop height, and a potential energy E [E = mgh (m: mass of solder, g: gravitational acceleration, and h: drop height] at the drop height is defined as the breaking impact energy.

[0075]

First, relationships between the composition ratio of Ge and the zero cross time Tb and between the composition ratio of Ge and the wet force F_2 are shown in Fig. 5.

[0076]

As shown in Fig. 5, the wettability, particularly, the zero cross time Tb of the solder sample is changed depending on the composition ratio of Ge. To be more specific, the zero cross time Tb is minimized when the composition ratio of Ge is 0.05 wt%, and is relatively short when the composition ratio of Ge is in a range of 0.01 to 0.1 wt%. As a result, it becomes apparent that the composition ratio of Ge may be desirable to be set in the range of 0.01 to 0.1 wt%.

[0077]

Next, relationships between the composition ratio of Bi and the zero cross time Tb and the composition ratio of Bi and the wet force F_2 are shown in Fig. 6, and a relationship between the composition ratio of Bi and the breaking impact energy is shown in Fig. 7.
[0078]

As is shown in Fig. 6, the wet force F_2 is not largely changed even when the composition ratio of Bi is increased, while the zero cross time Tb is largely changed depending on the composition ratio of Bi and becomes relatively shorter when the composition ratio of Bi is 0.5 wt% or less.
[0079]

As shown in Fig. 7, the breaking impact energy becomes smaller as the composition ratio of Bi becomes larger. To be more specific, when the composition ratio of Bi is 8 wt% or less, the breaking impact energy larger than 137 mJ (which is the breaking impact energy of the tin-lead solder) is obtained.
[0080]

Accordingly, to obtain a desirable wettability while ensuring a mechanical strength comparative to that of the tin-lead solder, the composition ratio of Bi is required to be in a range of 0.5 to 8 wt%.

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[0081]

Relationships between the composition ratio of Ag
and the zero cross time Tb and the composition ratio of
Ag and the wet force F_2 are shown in Fig. 8.

[0082]

As shown in Fig. 8, the zero cross time Tb rapidly
becomes short when the composition ratio of Ag is 0.5 wt%,
and the wet force F_2 rapidly becomes large when the
composition ratio of Ag is 0.5 wt%. Accordingly, to
obtain a desirable wettability, the composition ratio of
Ag is required to be 0.5 wt% or more.

[0083]

Fig. 9 shows a ternary phase diagram of a Sn-Bi-Ag
based alloy. In this diagram, the left side line of the
triangle designates the composition ratio of Ag, and the
right side line thereof designates the composition ratio
of Bi. A thick line extending downwardly, rightwardly
from a point at which the composition ratio of Ag is 3.5
wt% and the composition ratio of Bi is 0 wt% shows a Sn-
Ag binary eutectic line. When the composition ratio of Ag
is larger than a value on the line, coarsened acicular
crystals of Ag_3Sn are precipitated. As described above,
the suitable upper limit of the composition ratio of Bi
is 8 wt%, and the composition ratio of Ag at a point at

which the straight line representative of the composition

ratio (8 wt%) of Bi crosses the Sn-Ag binary eutectic

line is 3 wt%. To be more specific, when the composition

ratio of Bi is in the range of 0.5 to 8 wt%, if the

composition ratio of Ag is more than 3 wt%, crystals of

Ag_3Sn is precipitated. The crystals of Ag_3Sn are further

grown, and finally the above-described acicular crystals

of Ag_3Sn are precipitated, thereby degrading the

mechanical strength of the solder.

[0084]

Accordingly, to obtain a desirable wettability

while suppressing the precipitation of acicular crystals,

the composition ratio of Ag is required to be in a range

of 0.5 to 3 wt%.

[0085]

Next, relationships between the composition ratio

of Cu and the zero cross time Tb and the composition

ratio of Cu and the wet force F_2 are shown in Fig. 10.

[0086]

As shown in Fig. 10, the zero cross time Tb is

largely changed depending on the composition ratio of Cu,

and rapidly becomes short when the composition ratio of

Cu is 0.3 wt%. On the other hand, when the composition

ratio of Cu is more than 1 wt%, acicular crystals are

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precipitated, thereby degrading the mechanical strength of the solder.

[0087]

Accordingly, the composition ratio of Cu is desirable to be in a range of 0.3 to 1 wt%.

[0088]

From the above-described experiments, it is revealed that the suitable range of the composition ratio of each element in the Sn-Bi-Ag based alloy to which Ge and Cu are added is as follows:

Bi: 0.5 to 8 wt%

Ag: 0.5 to 3 wt%

Ge: 0.01 to 0.1 wt%

Cu: 0.3 to 1 wt%

Sn: balance

[0089]

Inventive Example 3-1

Granular ground metals of tin, zinc, indium, germanium, and silver were weighed in predetermined amounts shown in Table 5, and charged in a crucible. The ground metals were then melted and cooled in the same manner as that in Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Zn-In alloy to which Ge and Ag were added) was thus prepared. In addition, the

composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 6.

[0090]

Comparative Example 3-1

Granular ground metals of tin, zinc, and indium were weighed in predetermined amounts shown in Table 5, and charged in the crucible. The ground metals were then melted and cooled in the same manner as that in Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Zn-In alloy to which any additional element was not added) was thus prepared. In addition, the composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 6.

[0091]

Comparative Example 3-2

Granular ground metals of tin, zinc, indium, and germanium were weighed in predetermined amounts shown in Table 5, and charged in the crucible. The ground metals were then melted and cooled in the same manner as that in Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Zn-In alloy to which Ge was added) was thus prepared. In addition, the composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 6.

[0092]

Comparative Example 3-3

Granular ground metals of tin, zinc, indium, and silver were weighed in predetermined amounts shown in Table 5, and charged in the crucible. The ground metals were then melted and cooled in the same manner as that in Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Zn-In alloy to which Ag was added) was thus prepared. In addition, the composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 6.

[0093]

Comparative Example 3-4

Granular ground metals of tin, zinc, indium, and copper were weighed in predetermined amounts shown in Table 5, and charged in the crucible. The ground metals were then melted and cooled in the same manner as that in Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Zn-In alloy to which Cu was added) was thus prepared. In addition, the composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 6.

[0094]

Comparative Example 3-5

Granular ground metals of tin, zinc, indium, germanium, and copper were weighed in predetermined amounts shown in Table 5, and charged in the crucible. The ground metals were then melted and cooled in the same manner as that in Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Zn-In alloy to which Ge and Cu were added) was thus prepared. In addition, the composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 6.

[0095]

Comparative Example 3-6

Granular ground metals of tin, zinc, indium, germanium, silver, and copper were weighed in predetermined amounts shown in Table 5, and charged in the crucible. The ground metals were then melted and cooled in the same manner as that in Inventive Example 1-1. A solder ingot (solder sample composed of a Sn-Zn-In alloy to which Ge, Ag and Cu were added) was thus prepared. In addition, the composition of the solder sample, measured by the ICP-AES analysis, is shown in Table 6.

[0096]

[Table 5]

	Sn (wt%)	Zn (wt%)	In (wt%)	Ag (wt%)	Ge (wt%)	Cu (wt%)
Inventive Example 3-1	86.0	8.0	5.0	0.5	0.5	0.0
Comparative Example 3-1	87.0	8.0	5.0	0.0	0.0	0.0
Comparative Example 3-2	86.5	8.0	5.0	0.0	0.5	0.0
Comparative Example 3-3	86.5	8.0	5.0	0.5	0.0	0.0
Comparative Example 3-4	86.5	8.0	5.0	0.0	0.0	0.5
Comparative Example 3-5	86.0	8.0	5.0	0.0	0.5	0.5
Comparative Example 3-6	85.5	8.0	5.0	0.5	0.5	0.5

[0097]

[Table 6]

	Sn (wt%)	Zn (wt%)	In (wt%)	Ag (wt%)	Ge (wt%)	Cu (wt%)
Inventive Example 3-1	balance	8.5	5.3	0.5	0.03	0
Comparative Example 3-1	ditto	8.1	5.0	0	0	0
Comparative Example 3-2	ditto	8.6	5.1	0	0.05	0
Comparative Example 3-3	ditto	8.2	5.2	0.5	0	0
Comparative Example 3-4	ditto	8.2	5.0	0	0	0.4
Comparative Example 3-5	ditto	8.9	5.1	0	0.19	0.35
Comparative Example 3-6	ditto	7.8	5.1	0.5	0.04	0.44

[0098]

The wettability of each of the solder samples thus prepared was evaluated in the same manner as described above. The results are shown in Figs. 11 and 12.

[0099]

As is apparent from Fig. 11, for the solder sample composed of the Sn-Zn-in alloy to which Ag and Ge are added, the zero cross time Tb is shorter, the rising gradient of wet force is steeper, and the wet force F_2 is larger as compared with the solder sample composed of the Sn-Zn-In alloy to which any additional element is not added.

[0100]

As a result, it becomes apparent that the addition of Ag and Ge to the Sn-Zn-In based solder sample is effective to improve the wettability.

[0101]

Fig. 12 shows the wettability of the solder sample in which any additional element is not added, and also the wettability of each of the solder sample in which Ge is singly added, the solder sample in which Ag is singly added, the solder sample in which Cu is singly added, the solder sample in which Ge and Cu are added, and the solder sample in which Ag, Ge and Cu are added.

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[0102]

As is apparent from Fig. 12, the wettability of the solder sample in which Ag is singly added is not different from that of the solder sample in which any additional element is not added. Also, for each of the solder sample in which Ge is singly added and the solder sample in which Ge and Cu are added, the zero cross time is longer and the rising gradient of wet force is gentler as compared with the solder sample in which any additional element is not added. Further, for each of the solder sample in which Cu is singly added and the solder sample in which Ge, Ag and Cu are added, the zero cross time is long, the rising gradient of wet force is gentle, and the wet force F_2 is small.

[0103]

As a result, it becomes apparent that the wettability of the Sn-Zn-In based solder sample is rather graded by singly adding Ge or Ag or adding Ge or Ag in combination of another element, and the effect of improving the wettability is obtained only by adding the two elements Ag and Ge.

[0104]

[Effect of the Invention]

As described above, according to the present

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invention, there are provided a solder material composed

of a Sn-Zn-Bi alloy to which Ge and Cu are added, a

solder material composed of a Sn-Bi-Ag alloy to which Ge

is added, a solder material composed of a Sn-Bi-Ag alloy

to which Ge and Cu are added, and a solder material

composed of a Sn-Zn-In alloy to which Ge and Ag are added.

Each of these solder materials has a suitable melting

temperature, ensures good mechanical properties, and

exhibits a desirable wettability, and therefore, the

solder material, although being a lead-less solder

material, attains a good solderability comparable to that

of the tin-lead solder.

[Brief Description of the Drawings]

  [Fig. 1]

        A characteristic diagram showing a typical

relationship between the wet force and elapsed time,

obtained by a wetting balance method.

  [Fig. 2]

        A characteristic diagram showing the wettability

of each of a solder material composed of a Sn-Zn-Bi alloy

to which Ge and Cu are added, and a solder material

composed of a Sn-Zn-Bi alloy to which any additional

element is not added.

  [Fig. 3]

A characteristic diagram showing the wettability of each of a solder material composed of a Sn-Zn-Bi alloy to which Ge is singly added, a solder material composed of a Sn-Zn-Bi alloy to which Ag is singly added, a solder material composed of a Sn-Zn-Bi alloy to which Ge and Ag are added, a solder material composed of a Sn-Zn-Bi alloy to which Ge, Cu and Ag are added, and a solder material composed of a Sn-Zn-Bi alloy to which any additional element is not added.

[Fig. 4]

A characteristic diagram showing the wettability of each of a solder material composed of a Sn-Bi-Ag alloy to which Ge is singly added, a solder material composed of a Sn-Bi-Ag alloy to which Ge and Cu are added, a solder material composed of a Sn-Bi-Ag alloy to which Cu is singly added, and a solder material composed of a Sn-Bi-Ag alloy to which any additional element is not added.

[Fig. 5]

A characteristic diagram showing relationships between the composition ratio of Ge and the zero cross time Tb and between the composition ratio of Ge and the wet force F_2 for a solder material composed of a Sn-Bi-Ag alloy to which Ge and Cu are added.

[Fig. 6]

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A characteristic diagram showing relationships between the composition ratio of Bi and the zero cross time Tb and between the composition ratio of Bi and the wet force F_2 for a solder material composed of a Sn-Bi-Ag alloy to which Ge and Cu are added.

[Fig. 7]

A characteristic diagram showing a relationship between the composition ratio of Bi and a breaking impact energy for a solder material composed of a Sn-Bi-Ag alloy to which Ge and Cu are added.

[Fig. 8]

A characteristic diagram showing relationships between the composition ratio of Ag and the zero cross time Tb and between the composition ratio of Ag and the wet force F_2 for a solder material composed of a Sn-Bi-Ag alloy to which Ge and Cu are added.

[Fig. 9]

A characteristic diagram as a ternary phase diagram of a Sn-Bi-Ag alloy.

[Fig. 10]

A characteristic diagram showing relationships between the composition ratio of Cu and the zero cross time Tb and between the composition ratio of Cu and the wet force F_2 for a solder material composed of a Sn-Bi-Ag

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alloy to which Ge and Cu are added.

[Fig. 11]

A characteristic diagram showing the wettability of each of a solder material composed of a Sn-Zn-In alloy to which Ge and Ag are added, and a solder material composed of a Sn-Zn-In alloy to which any additional element is not added.

[Fig. 12]

A characteristic diagram showing the wettability of each of a solder material composed of a Sn-Zn-In alloy to which Ge is singly added, a solder material composed of a Sn-Zn-In alloy to which Ag is singly added, a solder material composed of a Sn-Zn-In alloy to which Cu is singly added, a solder material composed of a Sn-Zn-In alloy to which Ge and Cu are added, a solder material composed of a Sn-Zn-In alloy to which Ge, Ag, and Cu are added, and a solder material composed of a Sn-Zn-In alloy to which any additional element is not added.

[Abstract]

[Object] To provide a solder material having a suitable melting temperature, good mechanical properties, and a good wettability leading to a desirable solderability.

[Solving Means] Germanium and copper are added to a Sn-Zn-Bi based solder material; germanium is singly added, or both germanium and copper are added to a Sn-Bi-Ag based solder material; and germanium and silver are added to a Sn-Zn-In based solder material.

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Fig. 1

wet force

time

Fig. 2

  Wettability of Sn-Zn-Bi Alloy

wet force

time

without additional element

Fig. 3

  Wettability of Sn-Zn-Bi Alloy

wet force

time

without additional element

Fig. 4

  Wettability of Sn-Bi-Ag Alloy

wet force

time

without additional element

Fig. 5

zero cross time Tb (sec)

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composition ratio of Ge (wt%)

wet force F_2

zero cross time Tb

wet force F_2

Fig. 6

zero cross time Tb (sec)

composition ratio of Bi (wt%)

wet force F_2

zero cross time Tb

wet force F_2

Fig. 7

breaking impact force

composition ratio of Bi (wt%)

Fig. 8

zero cross time Tb (sec)

composition ratio of Ag (wt%)

wet force F_2

zero cross time Tb

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wet force F_2

Fig. 9

Ag (wt%)

Bi (wt%)

Sn-Ag binary eutectic line

precipitation of acicular crystal

Fig. 10

zero cross time Tb (sec)

composition ratio of Cu (wt%)

wet force F_2

zero cross time Tb

wet force F_2

precipitation of acicular crystal

Fig. 11

  Wettability of Sn-Zn-In Alloy

wet force

time

without additional element

Fig. 12

Wettability of Sn-Zn-In Alloy

wet force

time

without additional element